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Polyacrylic Esters for Plasticizers

Neutral, thermally and chemically stable, halogen-free, liquid polyacrylic esters were desired for evaluation as plasticizers and hydraulic fluids.

These polymers were prepared by polymerization of alkyl acrylates in isopropylbenzenes as solvents, with and without use of dodecyl mercaptan. Best results were obtained by conducting the polymerization in refluxing triisopropylbenzene. As much as half the product was distillable, and the distilled portions were further fractionated to obtain relatively homogeneous fractions.

Most of the products were compatible with polyvinyl chloride–acetate, especially the higher boiling distilled fractions. All were clear, thermally stable liquids with little color or odor (except those made with mercaptan). These properties, together with low ASTM viscosity-temperature slopes and a wide range of viscosities, suggest use of the materials as plasticizers, hydraulic fluids, and synthetic lubricants.

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Liquid Polymers of Acrylic Esters

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SEVERAL studies of vinyl polymerization have included production of polymers of low molecular weight, but relatively little attention has been devoted to their physical properties and practical utility, although it was expected that they would be useful as plasticizers, hydraulic fluids, synthetic lubricants, or corrosion inhibitors. Ali, Mark, and Mesrobian (*1*) prepared liquid polymers from several vinyl monomers, including butyl and 2-ethylhexyl acrylates, and evaluated them as plasticizers for vinyl chloride resins. To keep the degree of polymerization low, they used carbon tetrabromide or allyl chloride as a chain transfer agent. The resulting halogen-containing polymers were thermally unstable and relatively inefficient as plasticizers for polyvinyl chloride.

The purpose of the present work was to make halogen-free liquid polyacrylates in the hope that they would be thermally stable and perhaps more efficient as plasticizers.

Gregg and Mayo, who have done a great deal of work on chain transfer in polymerization of styrene, reported the transfer constants of a number of mercaptans (*3*) and hydrocarbons (*4*). It was expected that these chain transfer agents would show approximately the same relative effectiveness in the polymerization of acrylic esters as was reported by Mayo for styrene. For this reason and because of their effectiveness and availability, the isopropylbenzene family of solvents was chosen for this work. In addition, dodecyl mercaptan was used in some experiments.

POLYMERIZATION EXPERIMENTS

Table I summarizes the polymerization experiments. The ratio of solvent to monomer used was always 2 to 1 by volume. The catalyst in experiments 1 and 2 was benzoyl peroxide (0.6 mole % based on monomer); in experiments 3, 4, 5, and 14 no catalyst was used; in all others the catalyst was di-*tert*-butyl peroxide (1.0 mole % except experiment 7, where 3 mole % was used). In experiment 2 the temperature was kept at 80° C. and a nitrogen atmosphere was maintained in the apparatus; in all other experiments the polymerization was carried out under reflux.

In experiments 8, 9, 15, 16, and 21 the solvent was heated to near the boiling point; then the monomer, containing the catalyst, was slowly added from a dropping funnel. The temperature and rate of reflux were controlled by the rate of addition of monomer and by the heat input. In all other experiments the solvent, monomer, and catalyst were mixed, and then heated to reflux. The initial reaction was sometimes vigorous, requiring efficient reflux condensers. Polymerization was usually complete in 1 to 3 hours, as indicated by a reaction temperature equal to or slightly higher than the boiling point of the solvent being used. Sometimes it was necessary to distill out a few milliliters of volatile liquid, presumably produced by decomposition of the di-*tert*-butyl peroxide catalyst, before the temperature would rise to the expected point.

When polymerization was complete, the solvent and low-boiling products were distilled through a 24-inch Vigreux column at a final pressure of 0.5 to 1.0 mm. of mercury and a stillpot temperature of 225° to 240° C. The residues were then further stripped by heating to about 250° C. in an alembic-type still under a pressure of 0.02 to 0.10 mm. In experiments 9 and 16 this second stage of stripping was omitted; in experiment 13, the product was divided in half, and one half was further stripped to a final temperature of 295° C. at 0.08 mm. pressure. At 295° C. slight decomposition and discoloration became apparent. None of the other polymers showed evidence of decomposition during stripping.

The yield of polymer, distilled and undistilled, based on the monomer used, was usually considerably more than 100%. This was due to the well known fact that the chain transfer agent is incorporated into the polymer as an end group on the chains.

Table II gives some physical properties of the undistilled polymeric residues, prepared as shown in Table I. Viscosities were measured in Ostwald-type pipets up to a maximum of about 40,000 centistokes. The ASTM viscosity slopes were measured from the straight lines obtained by plotting viscosities at three temperatures on ASTM standard charts for high-range viscosity (D 341–43). These slopes compare favorably with those of some lubricating oils and hydraulic fluids and suggest possible use of the polymers in these fields.

The distilled material from several similar experiments was combined and fractionally distilled to obtain the more or less constant-boiling fractions whose properties are shown in Table III.

The material listed as butyl acrylate I was collected from experiments in which butyl acrylate was polymerized in triisopropylbenzene without use of mercaptan. That listed as butyl acrylate II was collected from experiments in which butyl acrylate was polymerized in *p*-cymene with use of dodecyl mercaptan. In fractionating the latter material the lowest boiling fractions partially crystallized. Recrystallization of the solid from heptane yielded large colorless crystals, having a melting point of 159° C., 89.9% carbon, and 9.9% hydrogen. Bicymyl has a melting point of 157° C., 90.2% carbon, and 9.8% hydrogen. Less than a gram of the compound was isolated. A similar hydrocarbon having a melting point of 116° to 118° C. was isolated in small yield from the low-boiling fractions of the product obtained in the polymerization of ethyl acrylate in cumene in the presence of dodecyl mercaptan. Reported values for the melting point of "bicumyl," 2,3-dimethyl-2,3-diphenylbutane, vary from 115° to 118° C.

These solvent dimers were observed and isolated only in those experiments in which dodecyl mercaptan was used.

Molecular weights of the polymers shown in Tables I and II, as well as the distilled fractions shown in Table III, were estimated. The results were somewhat erratic and contradictory, but they furnished some useful information.

If it is assumed that one and only one solvent molecule (in the absence of mercaptan) was incorporated into each polymer chain, the average chain length might be estimated from the isopropylbenzene content of the polymer as determined by elementary analysis, saponification equivalent, ultraviolet absorption, or other means. Such estimations were made for several of the polymers (Tables II and III). Under end-group analysis is shown the molecular weights calculated from ultraviolet absorption data on the assumption that each chain contained one, only one, triisopropylbenzene group and that the absorptivity of this group was unchanged when the group was incorporated into the polymer chain. It is evident that the estimated molecular

Expt. No.	Solvent	Mole Ratio Solvent to Monomer	Dodecyl Mercaptan Wt. %	Dodecyl Mercaptan Mole %	Reaction Temp., ° C.	Stripping of Polymer Temp., ° C.	Stripping of Polymer Press., mm.	Yield of Polymer[a], % Distilled	Yield of Polymer[a], % Undistilled
				Butyl Acrylate					
1	Cumene	2.0	0	0	150–154	240	0.01	4	89
2	*p*-Cymene	1.8	0	0	80	220	0.05	1	90
3	*p*-Cymene	1.8	0	0	158–175	220	0.05	5	88
4	*p*-Cymene	1.8	0	0	162–177	280	0.10	14	78
5	Triisopropylbenzene	1.2	0	0	175–241	253	0.03	28	83
6	Triisopropylbenzene	1.2	0	0	190–233	255	0.04	28	87
7	Triisopropylbenzene	1.2	0	0	190–239	255	0.04	31	88
8	Triisopropylbenzene	1.2	0	0	210–235	245	0.06	66	69
9	Triisopropylbenzene	1.2	0	0	216–247	245	0.5	25	105
10	*p*-Cymene	1.8	1.1	0.7	165–176	255	0.03	10	108
11	*p*-Cymene	1.8	3.3	2.1	165–178	255	0.03	14	93
12	*p*-Cymene	1.8	15.8	10.0	169–181	260	0.04	36	87
13	*p*-Cymene	1.8	31.6	20.0	166–181	255	0.05	61	75
						295	0.08	93	52
				Ethyl Acrylate					
14	Triisopropylbenzene	0.9	0	0	120–238	240	0.02	11	83
15	Triisopropylbenzene	0.9	0	0	175–237	245	0.06	59	75
16	Triisopropylbenzene	0.9	0	0	174–233	220	1.0	32	95
17	Cumene	1.6	3.6	1.8	120–150	259	0.03	8	
18	Cumene	1.6	18.0	9.0	120–155	255	0.05	32	92
19	Cumene	1.6	41	20	120–155	250	0.02	..[b]	...[b]
				90% Ethyl Acrylate–10% Acrylonitrile					
20	Cumene	1.5	19.7	9.0	112–152	220	0.02	18	109
				***n*-Octyl Acrylate**					
21	Triisopropylbenzene	1.7	0	0	184–245	230	0.2	9	117

Table I. Polymerization Experiments

[a] Yields based on monomer used; yields of distilled and undistilled portions were calculated separately.
[b] About one third of the product was accidentally lost before distillation; the ratio of distilled to undistilled products was 1.27 to 1.00.

in the range of a few hundred to about 6000, most being in the range of 1000 to 2000. This is the range that appears most interesting for plasticizers, lubricants, and hydraulic fluids, because it is high enough to produce extremely low volatility and migration and yet low enough to avoid high viscosity and difficulty in milling or incompatibility.

The data of Tables I and II show that the molecular weight of the polymer can be controlled within wide limits by varying the kind and concentration of the solvent or the temperature or by use of mercaptan.

Several experiments in which methyl acrylate or methyl, propyl, or butyl methacrylate was polymerized in various isopropylbenzenes, without mercaptan, resulted in only solid polymers, which were not further examined.

weights by end-group analysis shown in Table III are at least three times as high as the true molecular weights, and hence one or both of the basic assumptions are invalid.

The molecular weights shown in Tables II and III under light scattering were determined by the apparatus and method developed by Brice and coworkers (*2*). This method loses precision as molecular weights become lower; hence the results in Table II are probably more reliable than those in Table III. The latter are rather uniformly about half the molecular weights estimated by end-group analysis but are undoubtedly somewhat higher than the true molecular weights.

The most reliable estimate of molecular weight was obtained by the ebullioscopic method. Acetone was used as the solvent, and the results are believed accurate to ±10 units.

Other estimates of molecular weights were calculated from the saponification equivalents, hydrogen numbers, and carbon analyses given in Table II, but the results showed little agreement.

The molecular weights of the polymers examined were

Table II. Properties of Polyacrylic Esters

Expt. No.[a]	n_D^{20}	d_4^{20}	Viscosity, Centistokes 20° C.	40° C.	100° C.	ASTM Viscosity-Temp. Slope	Molec. Wt.[b]	Analyses Sap. equiv.	Carbon, %	H No.[c]
1	1.4673	1.0414	16,700	..	...	..	...	.....	65.8	5550
2	1.4690	1.0565	>40,000	..	...	..	....	.....	..	......
3	1.4686	1.0374	8,000	1790	120	0.52	6400	166	66.8	2560
4	1.4692	1.0413	12,000	..	...	..	...	.....	..	......
5	1.4689	1.0296	4,980	..	...	..	...	.....	..	......
6	1.4688	1.0300	7,350	1600	107	0.54	...	.....	...	......
7	1.4693	1.0304	7,870	..	...	..	....	......	..	......
8	1.4711	1.0194	1,210	311	25.9	0.64	2000[d]	162	68.7	3950
9	1.4739	1.0084	540	..	15.2	0.65	1340	......	..	......
10	1.4682	1.0357	8,380	...	...	..	...	.....	..	......
11	1.4688	1.0315	3,790	..	...	..	...	.....	..	......
12	1.4682	1.0171	1,020	..	...	..	....	1.38[e]	67.2	......
13	1.4670	1.0053	267	..	...	..	1500	2.42[e]	66.6	......
	1.4670	1.0127	508	160	19.5	0.68	...	1.97[e]	66.2	......
14	1.4721	.....	>40,000	..	...	..	...	.....	...	......
15	1.4759	1.0832	34,500	3630	87.3	0.72	2170[d]	141.6	64.4	866
16	1.4790	1.0684	6,460	..	34.9	0.71	1780	.....	..	......
17	1.4705	....	>40,000	..	...	...	...	.....	...	......
18	1.4698	1.0861	8,140	1330	61.4	0.65	.....	1.68[e]	60.7	......
19	1.4686	1.0618	1,360	..	...	..	...	.....	..	......
20[f]	1.4741	1.0779	17,900	..	...	..	...	2.15[e]	63.1	2.20[g]
21	1.4729	0.9528	332	106	13.8	0.64	2700	.....	..	......

[a] These numbers are the same as in Table I and same acrylates were used.
[b] By light scattering (*2*).
[c] Equivalent weight per double bond.
[d] By end-group analysis (ultraviolet absorption), the product of experiments 8 and 15 showed molecular weights of 4200 and 4350, respectively.
[e] Sulfur, %.
[f] Ethyl acrylate, 90%; acrylonitrile, 10%.
[g] Nitrogen, %.

EVALUATION AS PLASTICIZERS

Various samples of the polyacrylates were evaluated as plasticizers for polyvinyl chloride–acetate copolymer (95 to 5, Vinylite VYDR). The plasticized compositions (35% plasticizer) were compounded by milling, and tested as previously described (*5*).

Although most of the ethyl and butyl polyacrylates were compatible with the resin, the compositions were frequently hard

TABLE III. PROPERTIES OF DISTILLED POLYACRYLIC ESTERS

Acrylate	Fraction No.	Vol., Ml.	Boiling Range[a] ° C.	Boiling Range[a] Mm.	n_D^{20}	d_4^{20}	Viscosity, Centistokes 20° C.	Viscosity, Centistokes 40° C.	Viscosity, Centistokes 100° C.	ASTM Viscosity-Temp. Slope	Molecular Weight End-group analysis	Molecular Weight Light scattering	Molecular Weight Ebullioscopic
Ethyl[b]	3	45	70–76	0.01	1.4842	0.9542	28.7	11.9	2.53	0.89	990	...	309
	8	49	109–14	0.01	1.4819	0.9993	126	37.5	4.93	0.85	1250	...	355
	10	38	137–42	0.06	1.4770	1.0248	257	64.7	6.88	0.83	1650	...	434
	12	37	154–58	0.01	1.4765	1.0387	616	124	10.2	0.79	1930	950	...
	14	21	176–80	0.01	1.4762	1.0500	1350	240	14.9	0.73	2200	900	...
Butyl I[c]	3	52	134–36	0.4	1.4871	0.9301	38.3	15.3	3.04	0.87	940	...	267
	6	35	113–16	0.01	1.4820	0.9594	63.4	...	...	..	960	...	312
	9	44	120–24	0.01	1.4789	0.9639	79.5	29.7	4.86	0.79	1450	...	397
	11	36	121–26	0.01	1.4798	0.9665	101	...	...	..	1210	...	412
	14	35	160–65	0.01	1.4718	0.9886	114	...	...	..	1800	920	...
	16	41	169–71	0.01	1.4724	0.9910	170	...	...	...	2420	...	...
	17	41	171–75	0.01	1.4728	0.9917	184	58.4	7.76	0.74	..	...	...
	18	35	175–87	0.01	1.4718	0.9980							
Butyl II[d,e]	2	11	75–77	0.01	1.4885	0.9569	12.3	...	...	..	..	...	...
	7	30	115–17	0.01	1.4670	0.9508	18.3	...	2.67	0.74	..	...	...
	9	23	149–50	0.01	1.4680	0.9667	35.1	...	3.96	0.71	..	...	...
	12	16	155–57	0.01	1.4673	0.9676	....	...	...	..	..	...	...
	14	14	175–82	0.01	1.4675	0.9802	70.4	...	...	..	..	...	...

[a] Di-2-ethylhexyl phthalate boils at 122° C. (0.01 mm.).
[b] Distilled fractions of experiments 14–16 were combined (total, 390 ml.) and fractionated.
[c] Distilled fractions of experiments 5–9 were combined (total, 580 ml.) and fractionated.
[d] Distilled fractions of experiments 10–13 were combined (total, 152 ml.) and fractionated.
[e] C, H, and S analyses of fractions 2, 7, and 9 were: (2) 75.6, 10.0, and 0.77; (7) 70.2, 10.2, and 4.29; (9) 69.1, 9.9, and 4.44, respectively.

TABLE IV. POLYACRYLATES AS PLASTICIZERS FOR POLYVINYL CHLORIDE–ACETATE

Plasticizer Used: Polyacrylate	Plasticizer Used: Expt. No.	Plasticizer Used: Table No.	Properties of Plasticized Resin[a]: Compatibility	Tensile strength, lb./sq. in.	100% modulus, lb./sq. in.	Elongation, %	Brittle point, ° C.
Ethyl	15	I	C	3370	...	...	21
	16	I	C	3480	...	130	18
	18	I	C	3190	2570	260	13
	19	I	C	3500	2370	320	4
	20	I	C	3220	2780	270	13
	3	III	I	...[b]	...[b]	...[b]	...[b]
	8	III	I	2900	1970	270	−11
	10–12	III	C	3320	2200	330	0
Butyl	7	I	I	...[b]	...[b]	...[b]	...[b]
	9	I	C	2330	2040	170	4
	10	I	C	...[c]	...[c]	...[c]	...[c]
	11	I	C	...[c]	...[c]	...[c]	...[c]
	12	I	C	2310	2060	160	9
	13	I	C	2960	1730	320	−15
Butyl I	3	III	I	...[b]	...[b]	...[b]	...[b]
	9	III	I	2610	1580	310	−20
	16	III	C	3110	1800	380	−14
	18	III	C	2930	1780	340	−12
n-Octyl	21	I	I	...[b]	...[b]	...[b]	...[b]
Control[d]	..	..	C	2860	1240	320	−32

[a] Vinylite VYDR containing 35% plasticizer.
[b] Could not be milled.
[c] Too hard to test.
[d] 2-Ethylhexyl phthalate.

and boardlike, sometimes so hard that they could not be tested. Table IV shows results of these tests.

The ethyl polyacrylate appeared to be more compatible but less efficient than the butyl. The one octyl polyacrylate sample was completely incompatible. In both the ethyl and butyl polyacrylate series, compatibility, efficiency, and ease of milling increased with increased amounts of dodecyl mercaptan used in the polymerization, or in other words, with decreased viscosity and molecular weight. In the distilled fractions of the ethyl and butyl polyacrylates, however, compatibility and ease of milling increased with increased molecular weight, whereas efficiency increased to a maximum and then decreased somewhat. Probably the incompatibility and inefficiency of the lowest boiling fractions were due to the high percentage of end group of nonacrylate composition in these fractions. It seems likely that if distillable polyacrylates could be made without the formation of harmful end groups, they would be better plasticizers than the polymers thus far obtained.

Of all the polymers evaluated, the most promising were the high-boiling distilled fractions of the ethyl and butyl polyacrylates. Those boiling above di-2-ethylhexyl phthalate appear to combine many of the advantages of both the monomeric and the polymeric type of plasticizer.

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